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Encapsulation of pesticides in starch by extrusion

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Abstract

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Technology has been developed for using starch as a matrix-forming polymer to entrap or encapsulate a broad range of chemical and biological pest control agents. Starch-encapsulated chemical herbicides and pesticides are safer to handle and improve efficacy of pest control through better delivery to the target pest and through reduction in losses of chemical that normally occur through evaporation, leaching and light decomposition. Release of the active agent from the matrix can be controlled by manipulation of the matrix properties through chemical or physical treatments, incorporation of other additives or selection of processing conditions. Performing the encapsulation in a twin-screw extruder provides a highly efficient versatile and continuous process amenable to commercialization. Thousand pound quantities of three selected herbicides are being evaluated in a multi-state study in 1990 and 1991 for weed control and reduction in ground water contamination.

Herbicide; Insecticide; Entrapment; Groundwater; Pest Control

Introduction

Interest in natural products as annually renewable raw materials for industry has greatly intensified, especially during the last fifteen years. Although much of this interest can be attributed to the oil embargo of the early 1970s, the increased abundance of agricultural production beyond available markets has generated an oversupply of many commodities and with it a look to such commodities as raw materials for industry to develop new and expanded markets.

Starch is one of the natural materials that is receiving considerable attention in this renewable resource scenario due to its great abundance, ease of recovery from plant sources, low cost and its ready conversion chemically, physically and biologically into a broad spectrum of low molecular weight chemicals and high molecular weight polymers. The National Center For Agricultural Utilization Research (NCAUR), Peoria, IL, has as one of its major objectives the development of technologies that can lead to new products and new or expanded markets for starch, derived principally from corn. Research on starch, which makes up about 70% of the kernel's composition, includes enzymatic and microbial conversions, chemical and physical modifications, and composite systems containing starch with natural and syn-

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[1]The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

thetic polymers. Prime market targets are those presently served by some of the >90 million metric tons of synthetic organic chemicals and 27 million metric tons of synthetic polymers now derived from petroleum and natural gas produced yearly in the U.S.

Starch Matrix for Encapsulation

One of the research areas that shows considerable promise for a large new industrial market for starch is its use as a matrix forming polymer to encapsulate agricultural chemicals such as herbicides and insecticides (collectively referred to as pesticides). There is a need for improved pest control technology both to reduce losses in agricultural production and to reduce the negative environmental impact of chemical pesticides.

Technology has now been developed that addresses better targeting of pesticides and reducing their environmental impact. Starch-based formulations provide controlled release of chemical agents that improve the efficacy of pest control by keeping the pesticide targeted to the pest. Losses of chemicals that normally occur through volatilization, decomposition by sunlight and leaching by water are greatly reduced when applied encapsulated in starch.

Encapsulation via Extrusion Processing

During earlier studies at NCAUR, we established that a suitable starch matrix for encapsulation of pesticides could be formed upon solubilizing starch in an aqueous alkaline system and then crosslinking it after the pesticide had been added and well dispersed. Several different technologies were developed that varied in the methods of solubilization and crosslinking of starch, pesticide dispersion and recovery of the starch-encapsulated pesticide. With each of these technologies, granular products result wherein the pesticide is well dispersed throughout a continuous starch matrix as micron-size cells or domains. While many starch-encapsulated herbicides and insecticides were prepared by these methods and showed good performance in laboratory and field studies, acceptance by industry was minimal due primarily to the cost associated with the matrix forming processes. Need was identified to improve the economics by reducing or eliminating chemicals used to solubilize and crosslink starch, by increasing solids level during encapsulation and by developing a continuous process more amenable to commercialization.

Earlier in 1990 and 1991 we reported that solid and liquid pesticides were efficiently encapsulated in a starch matrix in a high solids, continuous process using a twin-screw extruder (Carr et al., 1990 and 1991; Trimnell et al., 1991; Wing et al., 1991). No additives are required beyond starch, pesticide and water although, if desired, other additives can be readily incorporated. Solids level (starch + pesticide) of up to 80% can be employed. Granular formulations that can result contain up to about 25% active agent, although for field applications, levels of 10–15% are mostly desired. The particles, while being hydrophilic and swellable in water, are insoluble due to reassociation (retrogradation) of amylose and amylopectin molecules that occurs rapidly upon cooling the extrudates, especially at the high starch:water ratio used. Particles of various mesh size for field application are prepared by grinding and sieving the extrudates after drying to about 10% moisture. Selection of the proper die and the use of a die face cutter can directly yield particles up to 20 mesh with no grinding being necessary.

Variables, including the type of starch (amylose/amylopectin content), form of the active agent (solid or liquid, technical or formulated), water solubility and volatility of the pesticide, extruder processing conditions (solids level, temperature profile, shear, die configuration, residence time), and particle size of the granular formulation all impact on pesticide release rate and pest control efficacy.

Extent of swelling in water is determined by the volume change when dry particles are placed in water for 24 h. Release rate is calculated from GC analysis of aliquots of supernatant taken periodically from particles suspended in water.

In 1990 at NCAUR we devoted considerable effort to the encapsulation of atrazine, alachlor and metolachlor — three herbicides used in large quantities in agricultural practices for weed control. These herbicides were selected for field evaluation in 1990 and 1991 in a multi-state study to compare starch-encapsulated products with standard commercial formulations for efficacy of weed control and reduced movement of the chemicals into ground water.

Each active agent was encapsulated in starch in a Werner and Pfleiderer ZSK 30 corotating, twin-screw extruder. The ratio of the barrel length to the screw diameter was 43:1. The processing section included 14 individual barrel sections that permitted excellent temperature control during extrusion. Each barrel section could be heated individually through an electric heater or cooled through chilled water passed through the barrel jackets (30).

Several procedures were used to prepare starch-encapsulated atrazine at levels of active agent of 5, 10 and 20% (Table 1). For some procedures powdered atrazine and starch were preblended and fed to the extruder where water was metered in at one of the barrel sections. In another procedure atrazine was fed into a barrel section after water had been added and the starch gelatinized. Various temperature profiles were studied with temperature in the various barrel sections ranging from as low as 30°C to 125°C. Water addition was controlled to provide a starch concentration (based on starch and water) of from 35 to 70%. Extrudates were dried and ground to the desired mesh size then evaluated for efficiency of encapsulation, degree of swelling in water and rate of release of active agent. As the amount of active agent to be encapsulated increases from 5% to 20%, the amount that can be extracted from or near the surface of the granules increases. At 5% addition about 6% is extracted with chloroform, while at 20% addition nearly 40% is extracted. Release of atrazine from the chloroform washed products was similar regardless of the level of active agent encapsulated.

Small but significant increases in release rates occurred as starch concentration was increased from 35 to 65%. The quantities released in 24 h increased from 1.1 to 1.5 g/100 g of product (Procedure 4a of Table 1). These data indicate that release rate and swellability of starch-encapsulated atrazine products in water are directly related, with both increasing

TABLE 1

Extrusion procedures for encapsulation[a]

Procedure no.	Material added position (Barrel section no.)			Extrudate			Barrel temp. (°C) zone no.							
	Starch	Atrazine	Water	Starch concn. (%)[b]	Atrazine (%)	Total solids (%)	1	2	3	4	5	6	7	8
1[c]	1	1	3	35–70	5–20	36–75	70	90	100	100	100	90	90	90
2	1	1	3, 7	20	5	21	80	100	125	125	100	100	80	80
3a[d]	1, 11	1	3	65	5[e]	66	70	90	100	100	50	70	90	90
3b[d]	1, 11	1	3	65	2.5[f]	66	70	90	100	100	50	70	90	90
4a	1	11	3	35, 65	5	36, 66	70	90	100	90	50	70	90	90
4b	1	11	3	35, 65	5	36, 66	70	90	100	90	50	30	30	30

[a]Using a ZSK 30 twin-screw extruder.
[b]Starch concentration = g of dry starch – (g of starch with 10% moisture + g of added water) x 100.
[c]Starch + atrazine preblend. Starch concentration was 35–65% for 5–20% atrazine and 70% for 5% atrazine.
[d]Starch + atrazine addition at BS 1 plus starch alone at BS 11.
[e]Starch concentration = 55% at BS 3–10 and 65% from BS 11 through last zone.
[f]Starch concentration = 35% at BS 3–10 and 65% from BS 11 through last zone.

as starch concentration increases.

Two liquid chloroacetanilide herbicides — alachlor and metolachlor — also were encapsulated in starch in the twin-screw extruder. Metolachlor was employed both as technical grade and as commercially formulated Dual. Starch was fed into the first barrel section followed by water metered in at barrel section 2 and the herbicide metered in at barrel section 3. The amount of water added was controlled to provide starch concentrations of 35, 50, and 65%. Herbicide added was kept at the 10% level. As starch concentration increased, swellability of encapsulated products increased slightly and efficiency of encapsulation decreased marginally. Almost the theoretical amount of added herbicide was recovered in the extrudates. Approximately 8–15% could be extracted with chloroform.

Scaled-up Production

The encapsulation process was scaled up on a 57 mm twin-screw extruder (ZSK 57) of the same type and design as the ZSK 30 except that the ratio of the barrel length to screw diameter was 30 rather than 43. In scale-up, starch was fed into barrel section 1 at 68 kg/h and water was fed into section 2 to provide 70% starch concentration. For the active agents, atrazine was preblended with starch, while alachlor and Dual were metered in at barrel section 3. A 10% level of each of the active agents was employed. Table 2 shows properties of the products made by scale-up.

Starch encapsulation was as efficient in the scaled-up process as in the ZSK 30 laboratory preparations. Although there was no attempt to maximize efficiency of encapsulation during scale-up, it appears there would be little difficulty in realizing 95% efficiency or greater with almost all active agents. Interestingly, while the atrazine product prepared in the ZSK 57 exhibited greater swelling in water than when prepared in the ZSK 30, the two liquid herbicides yielded products from the ZSK 57 with lower swelling than when made on the laboratory extruder. Metolachlor, which has the highest solubility in water of the three, released much more rapidly from the encapsulation matrix.

Soil Column and Field Evaluations

In earlier reports it has been shown that starch-encapsulated herbicides, prepared by procedures other than extrusion, perform well in the greenhouse and the field to reduce losses that occur with standard formulations through volatilization and leaching by water. Due to the recency of the development of the encapsulation technology with the extruder, these products have not as yet been thoroughly evaluated. However, from greenhouse bioassays, soil column studies and preliminary data from multi-location field trials, results indicate the products will provide good weed control while reducing the amount of herbicide that is leached into surface and ground water.

Soil columns, packed with a silt loam soil, were used to compare leaching of active agent from standard commercial formulations applied as emulsifiable concentrates (EC) with that from the encapsulated products from the extruder. With the same amount of active agent applied to the columns and with the same amount of

TABLE 2

Properties of starch-encapsulated products from scaled-up production

Active agent	% Encapsulated	% Swelling in water	% Released into water		
			(1 h)	(3 h)	(21 h)
Atrazine	94	340	4	12	40
Alachlor	93	180	11	23	46
Metolachlor	77	180	43	68	100

water subsequently applied, the active agent from the EC formulations moved about five times as far down the column as did the agent from the starch-encapsulated products.

Field trials at locations in several states were conducted in 1991 and the data are being collected and evaluated. The locations included sandy soils with low organic matter content and silt loam soils. Soil core samples were taken at different times to record movement of active agent. Fields were planted to corn and yields were recorded at harvest. Analysis of the soil cores is now under way and the data will be available in several weeks. From field studies conducted in 1990, downward movement of atrazine was significantly reduced with the starch encapsulated product. From the 1991 trials, yields of corn, which are a measure of weed control, showed no significant difference between treatments with commercial formulations and starch-encapsulated products.

Conclusion

Chemical pesticides are efficiently encapsulated within a starch matrix by a continuous process in a twin-screw extruder. Properties of encapsulated products can be varied though modification of extruder parameters. Starch encapsulated products show good potential for reducing losses of pesticide that normally occur through volatilization and leaching by water. Reduced movement of chemical pesticides into ground water appears promising with granular starch formulations.

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